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Potential hydrogen and non-condensable gases production from biomass pyrolysis: Insights into the process variables

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ABSTRACT

The objective of this paper is to develop more favorable hydrogen energy that holds the potential to realize zero-carbon emissions, thereby negating concerns over global warming and promoting an outlook free of the dependency on fossil fuels. Pyrolytic gas has much H_2, CO_2, CO, and light hydrocarbons, such as CH_4, C_2H_6, etc., as non-condensable gases (NCGs), which offer the potential for use in industrial, power and transportation fields. This paper emphasizes the influence of biomass characteristics and compositions, moisture content, particle size, heating rate, temperature, reactor system, and carrier gases and catalysts on the production of hydrogen and NCG. The composition of the NCGs varies widely depending on the properties of the biomass and moisture content, which play key roles on the mole fraction of hydrogen in the final products. A small particle size is favorable in the chemically controlled pyrolysis process for hydrogen production, while the reformation of NCGs into H_2 via a shift reaction is significant in increasing the total hydrogen formation in the presence of catalysts. A great deal of effort has been directed towards the system carrier gas in terms of hydrogen production, because it enhances the secondary decomposition reaction. Thermo-chemical and biological processes for hydrogen production from sustainable energy sources are also reviewed. In order to predict the maximum hydrogen formation of a given feedstock, the extent to which the processes are dependent on the heating rate and the temperature of the biomass in the reactor is investigated. It is our belief that this is a crucial assessment in establishing a link and developing a learning strategy between networks of biomass to hydrogen transformation-related activities and in assessing the current economic status of this pyrolysis process in achieving the ultimate hydrogen energy source.

Contents

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1. Introduction

With regard to the global depletion of fossil fuels and increasing environmental pollution, numerous endeavors have been attempted to advance technology and to find other renewable and environmental friendly energy sources [1]. The massive use of energy derived from fossil fuels contributes substantially to the release of greenhouses gases and toxic gases, such as CO_2, SO_2, NO_x and other pollutants, which causes many environmental problems such as acid rain [2,3]. With regard to these issues, some researchers have attempted to capture these toxic gases via hydration [4,5]. This study investigates and reviews developments in the quest for cleaner, renewable alternatives for the generation of heat and power from biomass [6–8]. Hydrogen is a latent and cleaner energy, which is considered as an alternative fuel for the future [9,10]. Amongst all conventional fuels, hydrogen holds the highest specific energy content (120 MJ/kg) and is the most widespread constituent in the Universe [11].

Biomass pyrolysis is a complex process in which several chemical reactions take place in both the gas and the condensed phase alongside the mass and thermal resistances involved in the pyrolysis process. Condensable vapor known as bio-oil, bio-crude, etc., and non-condensable gases (NCG) known as CO, CO_2, H_2 and light hydrocarbon gases (LHG), such as CH_4, C_2H_6, C_2H_4, etc., are generated by the pyrolysis process [12]. However, the total hydrogen production from the pyrolysis process is the sum of the synthesized hydrogen gas plus the hydrogen produced from the synthesized carbon monoxide via the water–gas shift reaction, and the LHGs play a key role in achieving this and hence, increase the efficiency of the process [13].

Quantitative information on the process variables, such as biomass composition, moisture content, particle size, heating rate, temperature and so on, is the basis for understanding the biomass thermal conversion pathways and in providing predictive gaseous products that can be used as clean fuels and chemical feedstock. Hydrogen yield and the distribution of NCG products are highly dependent on the feedstock type and quantity, as well as on the prevailing conditions of the reactor.

A key point related to thermo-chemical routes is that there is no practical and documented process for obtaining hydrogen from a biomass plant in terms of commercialization [14]. An economic survey showed that a plant efficiency of about 56–64% would be achieved, by means of the net higher heating value together with the hydrogen production cost (HPC), about 10–14 US$/GJ [15]. Gasification is a more mature technology than pyrolysis for hydrogen production and this process has to be recognized as a cost-effective and efficient pathway to generate fuel gas [16]. The economic analysis takes into account the feedstock costs when calculating the final fuel price, which is about 36–62% in the pyrolysis process [17]. The HPC from biomass by pyrolysis and gasification processes are expected to be in the range of 1.47–2.57 US$/kg and 1.44–2.83 US$/kg, respectively [18]. A capacity handling a quantity of 139,700 kg per day produces hydrogen at a price of 1.99 US$/kg by the gasification process, when the raw material cost is expected to be 46 US$ per ton on a dry basis [18].

In this paper, reports relating to the direct biomass pyrolysis process for hydrogen production and the consequent production of NCGs are classified and summarized according to biomass compositions, moisture content, particle size, heating rate, temperature, reactor, and carrier gas effect. It should be noted that there have also been studies focused on hydrogen production by pyrolysis using different catalysts with the aim of maximizing the final product. Therefore, this work is useful in addressing those new opportunities in the development of hydrogen energy for reducing emission problems, improving energy security and sustaining long-term future applications.

2. An overview of hydrogen production technology

Hydrogen is a colorless, tasteless, odorless gas, which is lighter than air and thus, rises in the environment. Hydrogen cannot be found in a free state in nature because it is very reactive and therefore, it is found in combination with other elements. Natural sources, for example, biomass, hydrocarbons, water, etc., are the major feedstock for hydrogen formation because these sources are widespread [19]. Table 1 shows the combustion and explosion properties of hydrogen [20].

Hydrogen energy delivers power with zero carbon emissions, a pollution-free environment, and clean fuels for industry, buildings and transport, which is why it appears as such a promising energy source. Hydrogen production has a chance to emerge as an important economic possibility in the near future. The key question is to determine from which source hydrogen can be produced in a sustainable manner in large quantities and at acceptable cost. An important aspect to avoid is that hydrogen becomes just a more expensive way of harnessing fossil fuels [21]. A hydrogen-based sustainable energy system is described pictorially in Fig. 1 [22]. As hydrogen could become the “next energy”, Fig. 2 illustrates the future that hydrogen energy could deliver.

Large-scale centralized power plants (LSCPs) and small-scale generation plants (SSGPs) are two distinct pathways by which to form hydrogen from biomass. Distributed generation, decentralized generation and embedded generation are other alternative classifications of SSGPs. It should be noted that LSCPs require distributed generation systems that operate nearer the point of use [23]; thus, LSCPs might become important in the longer time scale. Based on distributed generation pathways, hydrogen formation currently occurs mainly by means of the water electrolysis process, whereas hydrogen from natural gas (NG) and coal reforming processes are seen as medium-term policies [24]. From the aspect of transportation, the distributed formation of hydrogen offers advantages over centralized generation. Generally, centralized distribution encounters substantial infrastructure obstacles that are completely absent in the distributed generation process. It can be seen from Fig. 2 that larger amounts of hydrogen formation might be possible if based on a mainly large-scale hydrogen generation policy. Aside from the large-scale policy, biomass or existing fossil fuel with CO_2 sequestration should be understood as applicable to larger centralized hydrogen formation plants. It can be seen from Fig. 2 that distributed hydrogen formation should be implemented in the short and medium term.

Table 1
Combustion and explosion properties of hydrogen.

Properties	Hydrogen
Density (kg/m^3)[a]	0.084
Heat of vaporization (J/g)	445.6
Lower heating value (kJ/g)	119.93
High heating value (kJ/g)	141.8
Thermal conductivity (mW/cm/K)[a]	1.897
Diffusion coefficient in air ($cm^2 s$)[a]	0.61
Flammability limits in air (vol%)	4.0–75
Detonability limits in air (vol%)	18.3–59
Limiting oxygen index (vol%)	5.0
Stoichiometry composition in air (vol%)	29.53
Minimum energy of ignition in air (MJ)	0.02
Auto ignition temperature (K)	858
Flame temperature in air (K)	2318
Maximum burning velocity in air (m/s)[a]	3.46
Detonation velocity in air (km/s)[a]	1.48–2.15
Energy of explosion mass related g TNT (g)	24.0
Energy of explosion volume related g TNT (m^3)[a]	2.02

[a] Values are in at STP conditions.

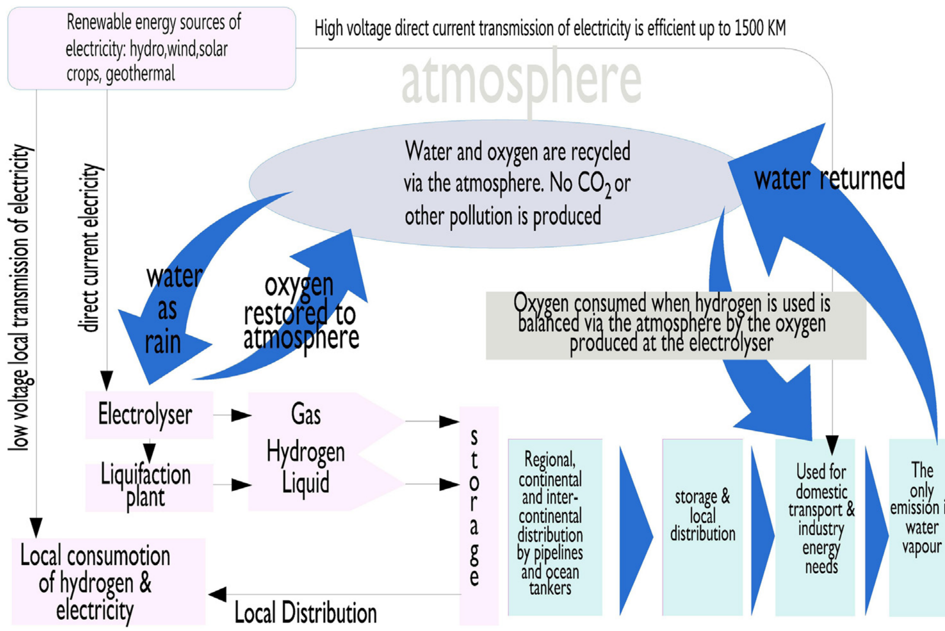


Fig. 1. Sustainable hydrogen production technologies.

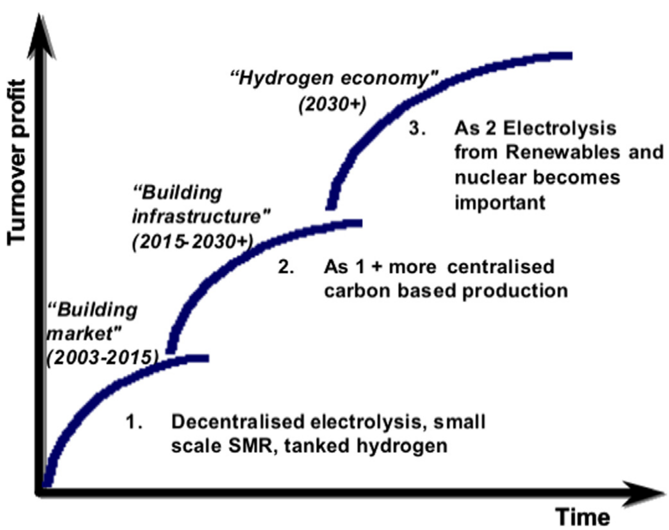


Fig. 2. Future hydrogen pathways captions [25].

Harnessing hydrogen from renewable biomass has a number of advantages and disadvantages with regard to fossil fuels, as shown in Table 2. The formation of hydrogen from biomass is lower owing to the lower hydrogen content (approximately 6% versus 25% for methane) and higher oxygen content (about 40% oxygen content) in biomass [26]. According to Konieczny et al. [27] natural gas contributes 48% hydrogen, oil provides 30% hydrogen and coal biomass delivers 18% hydrogen. The utilization of hydrogen gas as a potential fuel has faced two major problems: (1) unavailability of hydrogen in nature and (2) expensive production routes.

Hydrogen can be formed from biomass in a number of ways: (1) thermo-chemical (pyrolysis, conventional gasification, supercritical water gasification (SCWG)) and (2) biological (fermentative hydrogen production, photosynthesis, biological water–gas shift reactions (BWGS)). Existing hydrogen formation methods, such as combustion, incineration and catalytic hydro-treatment have also been recognized as potential procedures in the past, but unfortunately, these processes having limitations and are unsustainable owing to many problems, such as adulterated feedstock, intensive energy use, deactivation of employed catalysts, and char and tar formation [29].

The term "pyrolysis" is defined as a thermal degradation in the absence of oxygen, which converts a biomass into various intermediate products: solid (char), liquid (heavy molecular weight compounds that condense when cooled down) and gaseous products (light molecular weight gases) [30]. Although pyrolysis is considered as the precursor of gasification, it differs significantly from the gasification process. The pyrolysis process is brought about at 300–650 °C, whereas gasification occurs at temperatures of 800–1000 °C. The pyrolysis temperature ($T_{pyrolysis}$) is defined as the heating of biomass or an organic matter at a specified rate to a maximum temperature in the absence of air or oxygen and holding it there for a specified time. The formation of products from pyrolysis depends on several variables, such as the pyrolysis temperature, heating rate and so on. The primary products from pyrolysis comprise condensable gases and solid char. The condensable gases may decompose further into NCGs (CO, CO_2, H_2, and CH_4), liquid, and char through gas-phase homogeneous reactions and gas–solid-phase heterogeneous thermal reactions. In addition, NCGs, such as H_2, CO, CO_2, and LHGs are formed because of the cracking of condensable vapor through the gas-phase reactions [31,32]. A representative pyrolysis reaction is as follows:

$$C_nH_mO_p(\text{Biomass}) \xrightarrow{\Delta} \sum_{liquid} C_xH_yO_z + \sum_{gas} C_aH_bO_c + H_2O + C(\text{Char}) \tag{1}$$

Takes mass balance into account, the representative pyrolysis reaction is as follows [12]:

$$100\ \text{kg of Biomass} \xrightarrow{449-499\ ^\circ C} 60\ \text{kg Bio-oil} + 20\ \text{kg Char} + 20\ \text{kg NCG} \tag{2}$$

In all thermo-chemical conversion processes, pyrolysis plays a key role in the reaction kinetics and hence, in reactor design and in determining the product distribution, composition, and properties [33]. Given the concentration on temperature, heating rate and residence time of vapors, the pyrolysis process can be classified as slow, fast and flash pyrolysis. Furthermore, depending

Table 2
Some advantages and limitations of biomass as hydrogen resources [28].

Advantages of biomass to hydrogen	Limitation of biomass to hydrogen
Mitigating CO_2 emissions by using biomass	Higher handling costs and seasonal availability
With crop residue conversion agricultural output values increased	Solid char and tar generation
Sustainable biomass fuel appeared in place of fossil fuels	Process limitations: pressure resistance, crorosion, and hydrogen aging
Freed from municipal solid wastes costs	
Negligible amount sulfur, nitrogen, and metal content	

Table 3
Basic gasification reaction pathways for C_6 compound.

Reaction mode	Reaction Equation	Reaction number	Enthalpy (kJ/gmol)[a]
Pyrolysis	$C_xH_yO_z \rightarrow (1-x)CO + (y/2)H_2 + C$	(1)	180
	$C_xH_yO_z \rightarrow (1-x)CO + (y-4)H_2 + CH_4$	(2)	300
Partial oxidation	$C_xH_yO_z + (1/2)O_2 \rightarrow xCO + (y/2)H_2$	(3)	71
	$C_xH_yO_z + O_2 \rightarrow (1-x)CO + CO_2 + (y/2)H_2$	(4)	−213
	$C_xH_yO_z + 2O_2 \rightarrow (x/2)CO + (x/2)CO_2 + (y/2)H_2$	(5)	−778
Steam reforming	$C_xH_yO_z + H_2O \rightarrow xCO + yH_2$	(6)	310
	$C_xH_yO_z + nH_2O \rightarrow aCO + (x-a)CO_2 + yH_2$	(7)	230
	$C_xH_yO_z + (2x-z)H_2O \rightarrow xCO_2 + (2n + (y/2)-z)H_2$	(8)	64
Water–gas shift	$CO + H_2O \rightarrow CO_2 + H_2$	(9)	−41
Methanation	$CO + 3H_2 \rightarrow CH_4 + H_2O$	(10)	−206

[a] Enthalphy measured at 27 °C and $x=6$.

on the heating rate, pyrolysis can be divided into slow and fast pyrolysis. The process is known as slow when the time $T_{heating}$, required to heat the fuel to the pyrolysis temperature $T_{pyrolysis}$, is much longer than the characteristic pyrolysis reaction time T_r and vice versa [34]. So it can be written as – (i) slow pyrolysis when $T_{heating}, \geqslant T_r$ and (ii) fast pyrolysis when $T_{heating}, \lll T_r$. It can be argued that if the process is considered as a simple linear heating rate, then these criteria can be expressed in terms of heating rate. The characteristic reaction time T_r for a single reaction is taken as the reciprocal of the rate constant k, evaluated at the pyrolysis temperature [35].

Kasakura and Hiraoka [36] cited that a very small amount of LHGs with other major components, such as H_2 (5.5 vol%), CO (3.65 vol%), and HCN, nitrogen oxides, hydrogen chloride and sulfur oxides were produced during sludge pyrolysis in a pilot plant. The feasibility of producing hydrogen-rich fuel gas from pyrolysis and partial gasification was investigated by Xiong et al. [37], which showed that the yield of hydrogen increased with temperature. Depending on the type of dry biomass feedstock, it is noteworthy that when the temperature of fast pyrolysis increases, the formation of gaseous products increases and the formation of char and liquids decreases [38,39]. For example, the gaseous component increases to approximately 45–50% at 750 °C, whereas it is about 30–35% at 500 °C.

Demirbas and Arin [40] investigated the effects of temperature of the pyrolysis process on hydrogen yield and showed that hydrogen yield increased as a percentage of the total gases derived. A temperature change from 377 °C to 752 °C increased the hydrogen yield by the order of 27–41 vol% to 41–55 vol% of total gas based on feedstock. Di Blasi et al. [41] investigated the devolatilization role on the heating value of the producer gas by using different types of biomass, such as straw pellets, grape residues, beech-wood, and nutshells olive husks in a counter-current fixed bed reactor by pyrolysis. They showed that beech-wood would give lower quantities of gases (16.03 wt%), whereas an amount of 20.10 wt% was achievable for straw pellets. Davidian et al. [42] investigated hydrogen production from crude beech-wood oil using Ni/Al_2O_3 and $Ni–K/La_2O_3–Al_2O_3$ catalysts by pyrolysis process and found that a stoichiometric amount of 45–50% of hydrogen could be achieved together with carbon dioxide, carbon monoxide and methane gases.

Hornung et al. [43] investigated the pyrolysis of wheat straw at 450 °C in a fixed bed reactor with a flow rate of CG of 0.75–1.79 m^3/h for the production of hydrogen and other combustible components. They found that quantities of hydrogen, CO, CO_2, and CH_4 were expected to be 14%, 5–7%, 15–20% and 12%, respectively. Additionally, a total of 22% of gas was achieved by using a Ni-based catalyst. Li et al. [44] investigated the gaseous compound formation from legume straw in a free-fall reactor by fast pyrolysis at 800 °C. They reported that a particle size of 0.45–0.90 mm gave 28.2, 38.5, 15, 18, 5, and 8 mol% of hydrogen, CO, CO_2, CH_4, C_2H_6, and C_2H_4, respectively.

Biomass gasification is said to be an attractive option for transforming biomass into high-grade fuels. Generally, gasification is achieved at high temperatures, typically in the range of 800–900 °C in the presence of an oxygen/air steam. The process performs a series of consecutive reactions, which results in the conversion of carbonaceous feedstock into NCGs, such as H_2, CH_4, CO, CO_2, and H_2O. Table 3 shows the main gasification reaction pathways for gaseous energy production [45].

A number of feedstocks such as oil palm waste [46], meat and bone waste [47], wood sawdust [48], plastic residue [49], rich husk [50], pellets [51], etc., can be gasified to produce hydrogen as a cleaner energy source. A maximum amount of hydrogen would be obtained if the gasification process were subjected to the use of catalysts and therefore, Ni-based catalysts have been investigated with regard to reducing the tar content as well as increasing the hydrogen production [52]. Wu et al. [48] investigated hydrogen production from sawdust using a Ni/MCM-41 catalyst in a two-stage fixed bed reactor by a steam pyrolysis-gasification process. As the Ni loading was increased from 5 to 40 wt%, the hydrogen formation was raised by the magnitude of 30.1–50.6 vol%. Wu and Williams [53] investigated the catalytic performance on hydrogen production efficiency from polypropylene by gasification, using a laboratory-based two-phase reactor. They reported that hydrogen production was very effective in the presence of the Ni/Al_2O_3 catalyst, whereas $Ni/CeO_2/Al_2O_3$ was not productive during the experiments. Ruoppolo et al. [51] performed the gasification of

Table 4
Techno-economic feasibility of hydrogen from different production technologies [18].

Mode of Process	Raw material	Capital cost (M$)	Feedstock cost ($/GJ)	H_2 retail selling price ($/kg)	Carbon emissions[a]
Pyrolysis (low estimate)	Biomass	73.7	2.57	1.47	Zero
Pyrolysis (high estimate)	Biomass	4.2	0.92	2.57	Zero
Gasification	Biomass	167.5	2.81	1.99	Low
Gasification (low estimate)	Biomass	241.4	2.57	1.44	Low
Gasification (high estimate)	Biomass	8.8	0.92	2.83	Low
Steam methane reforming (SMR)	Natural gas[b]	94.4	10.55	2.48	Low
SMR with CO_2 sequestration	Natural gas	254.1	10.55	2.55	Significant
Coal gasification (CG) with sequestration	Coal	562.5	1.24	1.25	Low
CG without sequestration	Coal	495.0	1.24	1.05	Low
Advanced gasification with sequestration	Coal	1374.5	1.24	0.36	N/A
Electrolysis (near term)	Wind	3.0	10.56	5.55	Low
Electrolysis (long term)	Wind	0.9	10.56	2.27	N/A
Electrolysis (base load)	Nuclear	N/A	13.42	4.36	Low
Electrolysis (Off-peak)	Nuclear	N/A	13.42	7.36	Low
Power tower electrolysis	Solar	421.0	N/A	5.10	N/A

"N/A": Not available.
[a] Carbon emissions [73].
[b] Assuming natural gas costs $10.00 per MMBtu and all costs values in the table are presented in 2007 dollar by using the chemical engineering plant cost index.

wood, biomass, plastic, and olive husks for hydrogen formation using γ-alumina supported Ni-based catalyst in a fluidized bed gasifier both in the presence and in the absence of steam. The catalytic activity showed good results by a factor of 32 vol% of hydrogen formation. The catalytic activity was very high in the presence of steam and increased the hydrogen formation as well as decreased the tar content.

Asadullah et al. [54] reported the effects of catalysts on hydrogen production from cellulose at 450–550 °C using CeO_2, ZrO_2, Al_2O_3, TiO_2, MgO, and SiO_2 supported Rh catalysts in a laboratory-based fluidized bed reactor by gasification. They noted that a 1290 per μmol of hydrogen was achieved in the presence of Rh/CeO_2 and that this maximum amount of hydrogen was possible if the temperature increased. After their initial work, they investigated the catalytic performance of different types of $Rh/CeO_2/SiO_2$ catalysts on hydrogen production from cedar wood using a fluidized bed reactor at 550–700 °C by gasification process in the presence of air [55]. It was noted that the $Rh/CeO_2/SiO_2$ (35) catalyst showed better efficiency compared with the conventional Ni and dolomite catalysts for the conversion of carbonaceous compounds into hydrogen. They found that in presence of the $Rh/CeO_2/SiO_2$ (35) catalyst, the production of hydrogen, CO, CO_2, and CH_4 was expected to be 1535, 1387, 835, and 54 mmol/min, respectively.

Zhang et al. [56] carried out air blown gasification for hydrogen production from biomass in a pilot-scale fluidized bed reactor and investigated the effects of the variables of temperature, space velocity and steam/gas ratio. The authors believed that about 8 vol% of hydrogen concentration was achieved, which was later increased up to 30 vol% via the water–gas shift reaction. Lv et al. [57] presented an air-steam gasification process for hydrogen production from pine dust in a fluidized bed reactor, at 700–900 °C with the steam/biomass and equivalence ratio of 2.70 and 0.22, respectively. The authors suggested that hydrogen production increased from 22 to 71 g H_2 per kilogram following a temperature increase from 700 to 900 °C, together with production of 40, 20, 8, 0.15, and 3 g H_2 per kilogram of CO, CO_2, CH_4, C_2H_6, and C_2H_4, respectively. Marquevich et al. [58] performed catalytic steam reforming for hydrogen formation from sunflower oil, at a temperature of 800 °C in a fixed bed reactor. They highlighted that hydrogen, CO, CO_2, CH_4, C_2H_6, and C_2H_4 were found to be 72.87%, 18.1%, 10.7%, 13.4%, 3.2%, and 39.1%, respectively.

Much effort has been diverted to the investigation of hydrogen production from wet biomass in supercritical water conditions, although the principles and basic mechanisms of supercritical water gasification (SCWG) are not well acknowledged yet [59,60]. It adopts water as a reaction medium, owing to its specific transportation and solubilization properties and a feed with high moisture content (above 35%) can be used. A high temperature ($T_c > 374$ °C) and pressure ($P_c > 220$ bar) are needed to satisfy the minimum reaction conditions. At these conditions, biomass of high moisture content is dissociated rapidly at high efficiency into small molecules or gases within a few minutes.

Kruse et al. [61] described the SCWG of pyrocatechol in a tubular reactor at 700 °C in the presence of KOH and showed that hydrogen, CO_2, CH_4, and CO were found to be 7.8, 4.4, 0.8 and 0.17 mol/mol pyrocatechol, respectively, at 200 bar. They also reported that hydrogen yield is inversely proportional to pyrocatechol concentration, which means that water molecules release hydrogen atoms in order to motivate the intramolecular bond rupture of the reactant. Byrd et al. [60] investigated hydrogen formation from switchgrass biocrude by SCWG using Ni/ZrO_2, Ni/TiO_2, and Co/ZrO_2 catalysts at 600 °C and 250 bar in a laboratory-based reactor. A greater amount of hydrogen (0.98 mol H_2/mol C) together with a smaller amount of CH_4 was achieved in the presence of the Ni/ZrO_2 catalyst, whereas the Ni/TiO_2 and Co/ZrO_2 catalysts gave 0.67 and 0.68 mol H_2/mol C, respectively. Cao et al. [62] have investigated gaseous products from alkaline wheat straw pulping black liquor by SCWG at 400–600 °C, and residence times of 4.94–13.71 s under 25 MPa, in a continuous flow system. They showed that about 40.26–61.02%, 37.53–41.43%, 11.73–15.42%, and 0.14–1.51% of hydrogen, CO_2, CH_4, and CO, respectively, was found with increased temperature and residence time.

Sato et al. [63] reported on the formation of gaseous products from SCWG of lignin in a tubular reactor at 250–400 °C and water density of 0.3 g/cm^3. They highlighted that the amount of gases formed was enhanced with MgO supported Ni-based catalyst loading. At 400 °C and 10 wt% Ni/MgO loading, the hydrogen, CH_4, and C_2H_6 were found to be 11.7%, 37.2% and 0.2%, respectively. Demirbas [64] demonstrated the SCWG of fruit shells using an autoclave reactor at 377–477 °C and 23–48 MPa, and showed that as the temperature and pressure increased, the total gas yield also increased. Fruit shells, such as walnut, hazelnut, cotton cocoon, sunflower, and almond gave 61.3%, 63.5%, 64.7%, 65.7%, and 66.4%, respectively, at 477 °C.

The steam methane reforming (SMR) process is a commercially proven and cost effective method for syngas and hydrogen production from natural gas. SMR is the most practical technology currently available for hydrogen production and it occupies a share

of 40–50% of the total hydrogen production with an energy consumption rate of only about 1.23–1.35 GJ-NG/GJ-H_2 [65]. To date, SMR is the most mature technology, which requires high temperature and pressure to satisfy the minimum reaction conditions [66]. Based on dry feedstock, the SMR process produced hydrogen-rich gas that is typically of the order of 70–75% on a dry basis, together with smaller amounts of CH_4 (2–6%), CO (7–10%), and CO_2 (6–14%) [67]. Greatest difficulties in the SMR process are the reformers owing to their larger size, complex symmetry and greater expensive, and it is possible that some energy is lost during the conversion process [68]. However, much effort is being expended currently on the steam reforming of methane [69], ethanol [70] and methanol [71].

Coal gasification and water electrolysis are other options for hydrogen production. Coal gasification is relatively less mature than the SMR process. The main disadvantages of coal gasification are its complexity and expense, although this technology contributes 18% of the total hydrogen production, together with energy consumption of a magnitude of 1.54–1.69 GJ-coal/GJ-H_2 [65]. Electrolysis presents paths for hydrogen production that have several advantages, for example, water is much more abundant than hydrocarbons and hence, depletion and geopolitical concerns are fewer; the net energy costs of making hydrogen through electrolysis must be viewed in an economic context, and hydrogen can be produced from renewably generated electrical power [72]. Table 4 shows the hydrogen production costs for the various technologies. An overall idea can be visualized from this table that the potential costs of CO_2 sequestration and carbon emissions from these technologies are also affected by the hydrogen production.

It can be observed from Table 4 that HPC is the highest with solar, nuclear and wind energy, whereas coal and biomass sources of energy are the lowest. It is also apparent from Table 4 that hydrogen production from coal and natural gas is estimated to cost 0.36–1.25 $/kg and 2.48–2.55 $/kg for each energy source. Although it is obvious from the table that pyrolysis is less economical than gasification, pyrolysis receives greater credit in terms of carbon emissions with regard to its formation of co-products [74]. The cost of hydrogen production by pyrolysis ranges from 8.86 to 15.52 US$/GJ depending on the facility [74].

Pathways for making hydrogen by biological conversion are gaining interest because these processes seem to be environmentally benign and less energy intensive compared with thermo-chemical and electrochemical processes. Biological processes have three sub-categories: fermentative, photosynthesis processes, and biological water–gas shift reactions.

A hydrogen-producing enzyme, for example, hydrogenase and nitrogenase, is required to facilitate all the biological processes. Hydrogen via the fermentation process uses either anaerobic organisms or photo-fermentation, whereas in the presence of solar energy, phototropic organisms can generate hydrogen via the photosynthesis process. Furthermore, some photoheterotropic bacteria can easily stimulate water–gas shift reactions [24]. However, from a commercial point of view, the lower yields of H_2 and production rate are the main obstacles for these processes. Additionally, a very effective microbial culture is necessary to convert the waste material into a productive material, which is very complex in nature [75].

Das and Veziroğlu [76] presented a comprehensive review of a number of biological hydrogen formation pathways, including (i) photocatalytic degradation of organic compounds using bacteria, (ii) biophotolysis of water using algae and cyanobacteria, (iii) fermentative hydrogen formation from organic compounds, and (iv) hybrid systems. In hybrid systems, bacteria were used in the photosynthetic and fermentative processes. The findings of this investigation show that most biological methods are conducted at 30–40 °C under atmospheric pressure. From such findings, it was determined that photosynthetic hydrogen formation is lower than that of fermentative hydrogen formation.

Park [77] studied the fermentative hydrogen production from *Enterobacter* sp., *SNL*-1453, which was isolated from a domestic landfill area. The hydrogen yield was found to be 2614.5 mL/L in 17 h when the pH was set at 7.0. The hydrogen production rate increased with the increase of glucose concentration and showed that about 6.87 mmol per liter of hydrogen was achieved at a glucose concentration of 25 g glucose per liter. Datar et al. [78] reported that 11.6 mol of hydrogen may be acquired from 1 mol of glucose in the presence of pentose phosphate and hydrogenase from *Pyrococcus furiosus* enzymes in an in vitro system. They studied the anaerobic fermentative hydrogen production from corn stover with a residence time of 3–5 min using a 2.5-1 glass reactor. In that study, corn stover is subjected to water and acid impregnation within a pH range of 3.7–4 and 1–1.1, respectively. They found that approximately 432 mmol of CO_2 gas was released into the reactor at 138 mM glucose concentration when the *acetic* and *butyric acids* in the spent culture medium are 35.7 and 80.2 mM, respectively. At 35 °C, more than 65% of hydrogen can be attained from 16.5 mM glucose.

Eroğlu et al. [79] have presented details of anaerobic hydrogen production from olive mill wastewater (OMW) via dark-fermentation, followed by a photofermentation process using 55 mL glass vessels. Activated sludge and *Rhodobacter sphaeroides* O.U.001 cultures were used for the dark-fermentation and photo-fermentation processes, respectively. Hydrogen yield was found to be 29 L H_2/L OMW after photo-fermentation with 50 vol% of effluent of dark-fermentation with activated sludge. Lin et al. [80] carried out an anaerobic fermentation of glucose for hydrogen production in the presence of *C. acetobutylicum* M 121, *C. butyricum* ATCC 19398, *C. tyrobutyricum* FYa 102, and *C. beijerinckii* L 9 bacterium under reduced medium pH from 7.2 to a value between 4.6 and 5. They showed that the *C. beijerinckii* L 9 strains gave the highest hydrogen concentration (2.81 mmol H_2/mmol-glucose) among the tested strains.

Öztürk et al. [81] have presented the results of the photosynthesis of *Rhodobacter capsulatus* for hydrogen production under anaerobic conditions using photo-bioreactors. Maximum H_2 production rate was found to be 25 mL/L/h. They showed that the hydrogen production rate increased in the presence of cbb_3^- mutant, whereas it decreased by 3–4 times for modified electron carrier *cytochromes* mutant strains. Chen et al. [82] studied the photosynthesis of *Rhodopseudomonas palustris* using butyric acid,

Table 5
Biomass classifications and conversion products [33].

Biomass categories	Biomass type	Products
Materials (ligno-cellulosic)	Rice straw, cereal plants, bark, timber slash and mill scrap, wood, scrap, slash, husk etc	Ethanol, bio-liquid, and gas.
Agricultural residues	Cane sugar, food grain, wheat, corn, nutshells, hogs, poultry and manure from cattle etc	Ethanol
	Soya-bean, jatropha, sunflower, rape seed, canola, bluestem, poplars, etc	Biodiesel or bio-oil
Municipal waste	Sewage sludge, landfill gas, food waste, waste, paper, and yard clippings	
Industrial waste	Demolition wood, sawdust, waste oil or fat	

glutamic acid, and $FeCl_3$ mediums to investigate the hydrogen yield and maximum hydrogen production rate. Using response surface methodology, they found that H_2 yield and maximum hydrogen production rate obtained were 5.74 mol H_2/mol HBU and 24.9 mL/h/L, respectively, when optimal concentrations of 1832, 607 and 54 mg/L of butyric acid, glutamic acid, and $FeCl_3$, respectively, were used.

Only a very few efforts have been pursued for hydrogen production by biological water–gas shift reaction (BWGSR) process and it is still in a development stage [24]. In BWGSR process, some photo-heterotrophic bacteria, for example, *Rhodospirillum rubrum* can survive in the dark using CO as a sole carbon source and to generate ATP by coupling the oxidation of CO to the reduction of H^+ to H_2 [83]. Jung et al. [84] have presented the BWGSR process for hydrogen production from *Citrobacter* sp. Y 19 at 30–40 °C and pH of 5.5–7.5 under anaerobic conditions. They showed that H_2 yield was found to be 27 mmol/g cells h, which is about three times higher than *Rhodospirillum rubrum*.

3. Influence of different variables on hydrogen yield

Numerous variables, such as the composition of the biomass, moisture content, particle size, heating rate, temperature, reactor configuration, carrier gas flow rate, and the existence of catalysts affect the yield of hydrogen and the production of NCGs, via the appropriate process employed to achieve the desirable products. This following section will investigate the influence of those variables that control the process mechanisms, as well as provide the target product compositions.

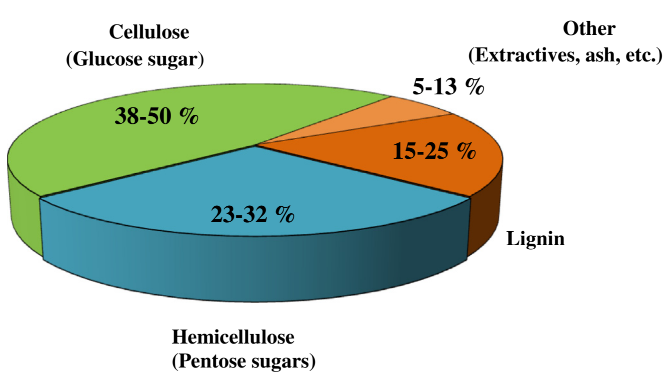


Fig. 3. Major biomass components [88].

3.1. Influence of biomass characteristics and compositions on hydrogen yield

Biomass is a biological material derived from living or recently living organisms or plants [85]. More simply, biomass is stored energy. In exploring biomass production and utilization, it is necessary to have a thorough understanding of the various types of biomass that can be used for heat, power, electricity, transportation fuels, and other byproducts. There are huge amounts of resources, co-products and waste that exist naturally, such as virgin wood, energy crops, agricultural residues, food waste, industrial waste and co-products, forest residues, municipal solid waste, and animal manure, which can be used as feedstocks for pyrolysis [86]. However, it is well understood that biomass extraction from natural resources must be accomplished in a manner that does not affect current food security or habitats, and shows (Table 5) that these resources are aggressively capable of nullifying CO_2, as well as producing potential bio-energy. It is essential to have sound knowledge of the physical and chemical properties of the biomass feedstock, because the characteristics of the biomass influence greatly on the performance of a biomass during pyrolysis [33].

The pyrolytic properties of biomass are controlled by the chemical composition of its major components, namely cellulose, hemicelluloses and lignin, and their minor components, including extractives and inorganic materials (Fig. 3). A series of complex, concurrent and consecutive reactions of these materials are followed during the pyrolysis process, which gives rise to a variety of products [87]. Owing to the different levels of interaction that might occur between the biomass components, the variation in chemical and physical properties of biomass materials make a significant difference to the corresponding pyrolysis profiles. In addition, the pyrolysis dynamics, such as initial degradation, conversion time, maximum volatile release rate, and its corresponding temperature, are of crucial importance in understanding the pyrolysis process for better production. Moreover, each of these properties, together with effective design and operation, represent the main theme required for full optimization of this process.

There are many studies on the pyrolytic nature of lingo-cellulosic materials, which includes a mixture of cellulose, hemicellulose and lignin, together with minor amounts of other organics. Table 6 represents some characteristics related to cellulose, hemicelluloses and lignin. It is worth noting that each of these components pyrolyze or degrade at different rates and by different mechanisms and pathways [89,90]. The interplay between the behavior of lingo-cellulosic materials and the ultimate products is strongly dependent on different factors. First,

Table 6
Characteristics of cellulose, hemicelluloses and lignin polymers and their products distributions [92,93].

Constituents	Formula	Characteristics	% (dry basis)		Products
			Hard-wood	Soft-wood	
Cellulose	$(C_6H_{10}O_5)_n$	Long chain polymer of linked sugars Higher degree of polymerization (~10,000) Higher molecular weight (~500,000) Highly insoluble and high strength	43	43	Condensable vapor and LHGs
Hemicellulose	$(C_5H_8O_4)_n$	Highly branched of sugars including xylan and glucommanan. Lower degree of polymerization (100–200) Random and amorphous structure with low strengths Easily soluble in weak alkaline	35	28	High NCGs and less tar
Lignin	–	Highly branched polymer of aromatic rings For cellulose fibers having cementing agent that holds adjacent cells together Highly insoluble	22	29	More aromatics and char

Table 7
Biomass compositions of some feedstocks.

Type of feed	C (wt%)[a]	H (wt%)[a]	N (wt%)[a]	S (wt%)[a]	O_2 (wt%)[a]	Ash (wt%)[a]	HHV (MJ/kg)	LHV (MJ/kg)	Ref.
Commercial beech (0.35 nm size)	50.8	5.9	0.3	0.02	42.9	0.4	N/A	N/A	[112]
Commercial beech (0.80 nm size)	50.4	5.9	0.3	0.02	43.3	0.4	N/A	N/A	[112]
Palm shell	49.74	5.32	0.16	0.16	44.86	2.1	N/A	N/A	[113]
Wood chip	49.7	6.4	0.1	< 0.1	43.8	0.3	19.3	N/A	[114]
Sawdust pellet	47	7.7	0.1	0	45.2	0.5	N/A	N/A	[115]
Corn stover	47.28	5.06	0.8	0.22	40.63	6	N/A	N/A	[116]
Corn cob	43.77	6.23	N/A	N/A	50	8.06	N/A	18.25	[117]
Olive stones	51.6	6	0.2	0.5	41.7	0.8	N/A	N/A	[118]
Wood sawdust	46.2	5.1	1.5	0.06	35.4	1.3	18.81	N/A	[119]
Legume straw	43.3	5.62	0.12	012	50.35	1.62	N/A	N/A	[120]
Olive bagasse	66.9	9.2	N/A	N/A	21.9	N/A	31.8	N/A	[121]
Corn stalk	43.65	5.56	0.01	0.01	43.31	5.58	N/A	17.19	[122]
Jute stick	48.0	9.0	N/A	N/A	45.1	0.33	22	N/A	[123]
Sugar cane bagasse	47.0	7.0	N/A	N/A	47.0	0.24	20	N/A	[123]
Cornhull	44.1	6.975	N/A	N/A	41.109	N/A	N/A	N/A	[124]
Corn stover	39.98	5.811	N/A	N/A	43.517	N/A	N/A	N/A	[124]
Oak	45.61	6.755	N/A	N/A	47.209	N/A	N/A	N/A	[124]
Autotrophic protothecoides	62.07	8.76	9.74	N/A	19.43	N/A	30	N/A	[125]
Heterotrophic *C. protothecoides*	76.22	11.61	0.93	N/A	11.24	N/A	41	N/A	[125]
Microalge	61.52	8.5	9.79	N/A	20.19	N/A	29	N/A	[125]
Coconut shell	92.28	1.09	0.47	0.04	3.08	2.78	N/A	N/A	[95]
Corn cob	86.38	1.20	0.56	0.05	5.34	4.31	N/A	N/A	[95]
Kukui nut shell	90.31	1.03	0.42	0.02	4.31	3.27	N/A	N/A	[95]
Leucaena wood	85.41	1.27	0.53	0.04	6.37	4.62	N/A	N/A	[95]
Macadamia nut shell	94.58	0.97	0.47	0.03	2.93	1.04	N/A	N/A	[95]
Oak board	91.50	1.22	0.18	0.01	3.55	1.04	N/A	N/A	[95]
Oak slabs	92.84	1.09	0.24	0.04	3.49	1.46	N/A	N/A	[95]
Pine wood	94.58	1.06	0.11	0.04	3.09	0.69	N/A	N/A	[95]
Rice hulls	52.61	0.82	0.57	0.06	3.87	41.34	N/A	N/A	[95]
Olive husk	47.4	5.8	1.4	N/A	36.3	3.6	N/A	N/A	[38]
Cotton cocoon shell	50.2	5.8	1.3	N/A	42.7	5.8	18.3	N/A	[38]
Tea factory waste	N/A	5.1	2.7	N/A	42.6	3.4	17.1	N/A	[38]
Almond shell	49.94	5.79	0.17	0.01	45.01	1.03	N/A	N/A	[95]
Bamboo	47.65	5.77	0.27	0.11	44.23	3.91	N/A	N/A	[95]
Garlic waste	37.85	4.97	0.49	0.22	43.12	17.07	N/A	N/A	[95]
Pecan shell	55.27	4.56	0.84	0.09	34.75	5.85	N/A	N/A	[95]
Walnut shell	49.95	5.87	0.13	0.13	42.52	2.02	N/A	N/A	[95]
Biomass	61.9	6	1.05	N/A	31	1.5	26.3	N/A	[126]
Fir	58.12	6.55	0.52	N/A	34.81	< 0.05	22.2	N/A	[126]
Beech	55.10	7.2	2	N/A	35.1	N/A	20.9	N/A	[126]
Wood	56.4	6.2	0.2	N/A	37.1	0.1	23.1	N/A	[126]
Hardwood (oak maple)	55.3	6.6	0.4	N/A	0.14	N/A	16.9	N/A	[127]
Scots	56.4	6.3	0.1	N/A	N/A	0.07	N/A	19.2	[127]
Wheat straw	58.4	6	0.1	N/A	N/A	0.09	N/A	16.6	[127]
Maize	46.9	5.4	0.2	N/A	47.4	2.9	N/A	15.4	[128]
Hardwood	54.5	6.4	0.18	N/A	38.9	0.16	17.5	16	[129]
Oak wood	46.3	6.8	0.1	N/A	46.8	0.05	N/A	N/A	[130]
PRB coal	66.0	5.0	0.9	0.99	15.98	11.3	27.0	N/A	[35]
Animal waste	43.0	6.0	3.0	0.2	31.0	18.0	17.5	N/A	[131]
Red wood	53.5	5.9	0.1	N/A	40.3	0.2	21.028	N/A	[131]
Rice straw	40.1	4.9	0.5	N/A	39.8	15.5	15.379	N/A	[131]
Sawdust	46.2	5.9	N/A	N/A	45.4	1.0	20.502	N/A	[139]
Municipal solid waste	48.0	6.1	1.5	0.2	33.0	12.5	20.0	N/A	[132]

"N/A": Not available.

[a] Dry basis.

carbon, hydrogen and oxygen are the main constituents that make up the biomass as a complex mixed polymer [91]. The second takes into account the presence of functional groups, and the third is based on the biomass formed from cellulose, hemicelluloses and lignin [91].

However, to date there is no model that predicts yield and composition of the final pyrolysis products, largely because of component interaction and the influence of mineral matter [94]. Apart from this argument, Antal and Grønli [95] investigated that char yields increase in some circumstances owing to the minerals present in the biomass, such as alkali metals, which show great catalytic effect on pyrolysis reactions and ash that also contributes to the same effect. Mineral materials also affect the reactivity and the ignition properties of the char. A literature survey showed that if the mineral concentration is higher in the biomass, then the process is exposed to the following trends: (i) degradation rate is higher, (ii) liquid yield is lower, (iii) char yield is higher, (iv) total gas yield is higher, and (v) H_2 and CO_2 yields increase while CH_4 and CO yields decrease [96,97].

Several researchers have investigated the influence of biomass characteristics on the hydrogen production and sole production of NCGs. Kalinci et al. [98] showed that the gas composition and the energy content of the fuels depend greatly on feedstock's composition. This might be because the different biomass feedstocks have different compositional structures, namely cellulose, hemicelluloses and lignin, which have different pyrolysis characteristics [44]. Li et al. [44] reported fast pyrolysis of biomass at 500–800 °C and found that hydrogen production is high in

biomass composed of greater amounts of cellulose and hemicelluloses than lignin. It was also found that woody biomass appears to have a higher potential for hydrogen production compared with agricultural residues [99]. This is relevant to the moisture content of agricultural residues when used as a feedstock. The higher moisture content in agricultural residue reduces the mole fraction of the combustible components owing to the large amount of air required to maintain the higher reaction temperature in the gasification process. This leads to a reduction of the heating value as well as the second law efficiency [100].

Depending on the biomass hydrogen-to-carbon (H/C) ratio, the composition of the biomass has significant influence on the pyrolytic yield. Kumar et al. [101] determined the following preferred decomposition temperature ranges for the initiation of pyrolysis for some selected lingo-cellulosic biomasses: hemicellulose, 150–350 °C; cellulose, 275–350 °C; and lignin, 250–500 °C. It can be inferred that cellulose and hemicellulose produce more hydrogen-rich gas than lignin [44]. Generally, cellulose turns into condensable vapor during pyrolysis. In contrast, hemicelluloses produce more NCGs and less tar than cellulose [102]. It is universally agreed that cellulose and hemicellulose are composed of linked chain sugar rings and that it is expected that LHGs will be generated during pyrolysis [103]. On the other hand, lignin degrades slowly owing to the high aromatic content causing the formation of char.

Without a catalyst, pyrolysis of pure cellulose converts predominantly to a monomer, levoglucosan. Levoglucosan vaporizes above 500 °C with char formation, which causes gas generation [104]. Lignin decomposes within the range of 280–500 °C, which is comparable to cellulose and releases at the maximum rate between 350 and 450 °C [105]. Moreover, Soltes and Elder [106] described that cellulose produced fewer aromatics and char than are produced by lignin pyrolysis. Under a slow heating rate at 400 °C, it yields about 40% of its weight as char [107]. Lignin also contributes to the liquid yield (~35%), as aqueous components and tar components. Furthermore, by the cleavaging of ether and carbon–carbon linkages it generates phenols [108]. It was observed that only 10% of the original weight of lignin turns into gaseous products via lignin pyrolysis. Many investigators [109–111] concluded that lingo-cellulosic materials are difficult to study because lingo-cellulosic materials have varied compositions. Table 7 shows the summative composition and heating values of some biomass products. It can be seen from Table 7 that the "proximate" analysis gives ash (mineral) and high heating value (HHV) based on the complete combustion of the sample to carbon dioxide and liquid water. Low heating value (LHV) gives heat release when the hydrogen is burned to gaseous water, corresponding to most heating applications. The "ultimate analysis" gives the composition of the biomass in wt% of carbon, hydrogen and oxygen (the major components) as well as sulfur and nitrogen (if any).

3.2. *Influence of moisture content on hydrogen yield*

In the sense of moisture content (MC), ligno-cellulosic materials carry lower than 50% lignin and moisture; agricultural products carry lower than 20%, and aquatic biomass is characterized by a very high MC [133]. However, it was realized that moisture embedded cellulose degrades more slowly than dry cellulose within the temperature range of 100–150 °C [134]. Similarly, Mok and Antal [135] reported that if cellulose contains higher MC, then the relevant products are increased with a decreasing pyrolysis temperature. Bridgwater [136] showed that the water content in feedstocks during pyrolysis was typically 12 wt% of dry feed. They also pointed out that about 10% MC was generally required for the fast pyrolysis process, whereas slow pyrolysis could be slightly more flexible for MC [137]. However, in the case of wood pyrolysis the MC range is typically about 15–20% [138]. Additionally, bed temperatures remain approximately stable with MC values below 15% [139]. Nevertheless, the MC level of the biomass depends on the gasifier in which it is to be processed; in updraft-type reactors, it could be as high as 50% [21]. The higher MC in biomass is responsible for the reduction of H_2 and CO formation, whereas CO_2 formation is enhanced. Moreover, the higher MC reduces the temperature, which also plays a key role in the product distribution [140]. It can be inferred that the presence of water content increases the volatile yield owing to the radicals from the thermal decomposition process being stabilized [141].

A very wide range of differences because of the MC effect was highlighted Furness et al. [142]. They generalized that excess water or higher MC affects the process efficiency and gas compositions, and that higher water content in the feedstock causes an increase in the production of hydrogen and methane. The influence of MC in raw biomass was also investigated by Plis and Wilk [100] who found that the CO content in the syngas is higher in the case of dry fuels, whereas the CO_2 content increases with increasing moisture in the feedstock. Additionally, higher MC in the biomass reduces the molar fractions of the combustible components and the efficiency of the process. In order to examine the effects of biomass MC on syngas, Antonopoulos et al. [143] developed a non-stoichiometric model for a downdraft gasifier using olive wood, miscanthus and cardoon. The increase in biomass MC decreases the lower heating value (LHV) of the produced gas. A 40% increase in fuel MC results in an approximately 1 MJ/m^3 reduction of the LHV of the synthesized gas. Pérez et al. [144] experimented with a downdraft reactor and pine bark as the feedstock, and concluded that the optimum fuel MC level was 10.62%. Hosseini et al. [145] conducted a thermodynamic analysis of the effects of MC on the exergy efficiency of gasification with air and steam with sawdust. When the moisture fraction of the feed biomass entering the gasifier was increased from 0.15 to 0.25 (kg of moisture to kg of wet biomass) the exergy efficiency of the steam-biomass gasification process decreased from 17.8% to 16.4%. This change was from 19.1% to 18.4% for the air-biomass gasification process.

Kalinci et al. [26] also showed that the moisture of fuel causes an increase in the amount of hydrogen and LHGs. In addition, for any thermal processing system, it is necessary that biomass MC should be minimized as required. Hence, the thermal efficiency of the system could be increased by operation at lower temperature, which would evaporate a portion of the biomass moisture. To remove MC from the feedstock requires more energy to overcome the absorption energy, because most biomass is hygroscopic and water is more endothermic [146]. Some biomass shows tremendous MC, as high as 90% (dry basis) [147]. Table 8 presents some biomass MC. Moreover, the oxygen content in biomass has an overall range from 40 to 45 wt% [148]. Ni et al. [24] found that if the MC is greater than 35%, then supercritical water is considered

Table 8
Some biomass moisture content [34].

Biomass	Wood bark	Corn stalks	Wheat straw	Sawdust	Food waste	Rice husk	Rice straw	Dairy cattle manure	Water-hyacinth	RDF pellets
Moistur content (wt%)	50–80	40–60	8–20	25–55	30–60	88	7–10	70	95.3	25–35

as a biomass gasification process and smaller molecules or gases develop within a few minutes from biomass decomposition at above critical temperature of 647 K, and critical pressure of 22 MPa. Nevertheless, it can be seen that consistency of these observations is necessary for better understanding of the pyrolysis process, which could go a long way towards improved production of hydrogen and NCGs.

3.3. Influence of particle size on hydrogen yield

Expertise from different schools of thought is being applied to the effects of particle size (PS) on the pyrolysis process, elucidating the impact it has on hydrogen and LHGs production. If PS is increased, then liquid yields reduce and hence, secondary cracking reactions within the particle increase as the temperature increases as well as hydrogen and LHGs increases [149,150]. PS plays a key role on the gas formations that depend on process temperature. For example, different PS was investigated during liquid fuel productions, but these particles not only reduced the char formations but also increased pyrolysis conversion that ultimately increased the hydrogen and LHGs [151,152]. As with larger PSs, more char is formed through restricting the rate of disengagement of the primary vapor products; hence, increasing the scope for secondary cracking reactions, which means that the gas yield is increased, as highlighted by Antal et al. [95]. Apart from larger PS, the escape of condensable gases from the reaction zone before undergoing secondary cracking, depends greatly on finer biomass particles, because these particles offer lower resistance and liquid products are usually formed. However, the escape of the primary pyrolysis products from the reaction zone is facilitated by larger PSs, because these particles offer higher resistance. On the other hand, coarse particles offer lower thermal conductivity (~0.1 W/mK) and hence, the interior side of the biomass particles could be heated at a slower rate, whereas the exterior surface could be heated as fast as 1000 °C/s.

The secondary reactions could be high as the interior surface associated with slow heating rate when PS remarkably larger because such conditions significantly favor hydrogen and LHGs formations rather than liquid production [149]. If PS ranging from 0.3 to 1.5 mm can be used for pyrolysis of biomass, then the yield of oil would be reduced [153]. Aside from such argument, Seebauer et al. [154] pointed out that experimental results do not rely on PS during biomass pyrolysis. Nevertheless, if the particle size is coarser, then more gaseous product is formed. At a given temperature, the yield of gas and composition is enlarged with a decreased manure particle size [155].

The yield of gas varies when the PS fraction changes greatly at the same temperature. For instance, the yield of gas is increased from 0.51 m^3/kg at 900 K to 0.81 m^3/kg at 1010 K when PS is small. On the other hand, at the same temperature, the yield of gas increased from 0.10 to 0.60 m^3/kg when PS is large. The formation of hydrogen and other gases is favored by a smaller size of biomass particle [44]. In addition, if the biomass particle is small, then the generation of char and liquid could be reduced. The quantity of products is related to the smaller PS, because a lower space residence time or a reduced reactor size could still facilitate the complete cracking of the heavier and condensate fractions [156]. In addition, Wei et al. [120] reported the effect of PS in the pyrolysis process in a free fall reactor, and they pointed out that smaller particles lead to an increase in the gas yield. They found that as the PS decreased (smaller than 0.20 mm), the biomass is pyrolyzed adequately at 800 °C and more volatiles are released, which leads to a higher production of H_2 and CO.

Encinar et al. [157] investigated the effects of PS between 0.4 and 2 mm on gas production with the temperature range of 300–800 °C and showed that 3.92, 1.99, 3.82, and 5.56 mol/kg of biomass was produced for hydrogen, methane, carbon dioxide, and carbon monoxide, respectively, during Cynara pyrolysis. On the other hand, Commandré et al. [158] studied the influence of PS in the ranges of 80–125 and 160–200 μm at 650–950 °C with a rapid heating rate ($> 10^3$ K/s) during the pyrolysis of wood and showed that PS has a lesser impact on the products.

Biomass particles are rarely spherical or even cubicle, but tend to have a length that is several times larger than the thickness or the width, i.e., a pin chip. There is a misleading tendency to report that the maximum particle dimension as the nominal particle size. However, the parameter that is normally of interest with respect to the heating rate of a particle and to fast the surface area per unit weight. It can worth be noted that the temperature and PS does not affecting the particle residence time as well as the formation of gas for a given PS rather it depends on the type of reactor [112].

3.4. Influence of heating rate on hydrogen yield

The yield of the desirable products and composition of those products depends solely on the length of the heating rate (HR) of the biomass particle. The HR can be considered as a function of temperature and residence time. Higher residence times have a tendency to decompose secondary reactions of hydrocarbons in the pyrolysis-volatiles to accumulate as LHGs. Many studies have revealed that the catalytic heterogeneous reactions between the carbon-based materials and pyrolysis-volatile form H_2 gases. The beneficial feedback from this heterogeneous reaction is that it proceeds rapidly because of longer residence time and converts part of the aliphatic compound into gaseous products, such as H_2 and CO [29,159]. In addition, this rapid heterogeneous reaction rate is responsible for enhancing the H_2 and CO in pyrolysis-gases, while the percentage of both CO_2 formations and aliphatic hydrocarbon is decreased at higher temperatures with a low N_2 purge rate and feedstock rate. Furthermore, a higher percentage of H_2 and CO is achieved because char formation and accumulation within the reactor reflects the catalytic effect on these heterogeneous reactions, which leads to lower generation of LHGs, such as CH_4, C_2H_4, C_2H_6, etc. [160,161].

With increasing HR, the yield of volatile products such as gases rises because of the decline of solid residues. In addition, within the temperature range of 475–525 °C, the residence time of gas is reduced with an increasing HR [162]. The advantages of these gaseous fuels are that they are high in hydrocarbons with high calorific value [161]. Most of the gas-forming reactions proceed at higher temperatures. Apart from this characteristic, a lower HR could possibly provide an opportunity for the gases to escape from the reaction zone, although this only happens when the gases have sufficient time before cracking the secondary reactions. The low HR is a result of the impact of the particle size on the pyrolysis process.

With increasing PS, the rate of thermal diffusion within a particle is reduced. Although liquid products are formed at higher HR and higher temperature with small particles, char formation exhibits the opposite trend. For instance, Debdoubi et al. [163] observed that the liquid yield increased by nearly 24% for Esparto biomass when the heating rate was changed from 5–250 °C/min to 400–500 °C/min. Secondary char forms due to the gradual removal of volatiles from the reactor at slow HR. As pyrolytic reactions vary with temperature, the transformation and decomposition of the earlier products from the biomass proceed through a series of consecutive reactions.

Moreover, products formation increases as the secondary reactions heating the initial products continuously. The secondary reaction reduces when heating rate (in case of flash pyrolysis) is rapidly applied for a long time. As a result, decomposition of earlier products can be increased and no char is formed. With

Table 9
Operating conditions in a pyrolytic reactor.

Mode of products	HR	Temperature	GRT
Production of char	Slower	Lower	Longer
Production of liquid	Higher	Moderate	Shorter
Production of gas	Lower	Higher	Longer

"HR and GRT": Heating rate and gas residence time respectively.

increasing residence time, secondary reactions of hydrocarbon in pyrolysis-volatiles increased as well as NCGs [29]. Zuo et al. [164] investigated the gaseous products (especially H_2 and CH_4) of the pyrolysis of fir wood and found that they are increased with a change of HR from 1 to 6 °C/min. More simply, the formation of gaseous products, such as hydrogen and LHGs, increases with a higher HR [165].

If the desirable products are liquid, then minimizing the extent of secondary reactions by cooling the primary vapors causes a rapid HR in fast pyrolysis [137]. Total yield of volatile matter increases by about 11% with bituminous coal when the HR is increased from 1 to 104 K/min using different types of reactors [166]. At lower temperatures with higher HRs, the residence time for biomass is short, which results in a shorter time for the dehydration reactions. In addition, at lower temperatures, less water is lost, which is why more cellulose and lignin will be decomposed easily. The beneficial feedback of this easier decomposition is higher yields of gaseous products as well as low char formation [167]. In addition, primary volatile products are exposed owing to the rapid heating, but conceptually, a more stable anhydro-cellulose is formed from cellulose dehydration owing to the lower HR, which gives higher char yield [168].

Pyrolysis reactions are known as endothermic reactions, which is why they need a high heat flux. For this purpose, a rapid heat transfer rate could be essential for agitating the particles sufficiently as quickly as possible [136]. To achieve this, heat fluxes of 50 W/cm^2 would be required, but it is not mandatory or practicable for a commercial process [169]. Giudicianni et al. [170] investigated the degradation pattern at different temperatures during the thermal analysis of cellulose degradation. They pointed out that the primary degradation at above 450 °C would produce condensable volatiles and that these volatiles undergo further secondary decomposition. These secondary reactions are responsible for the release of CO, CH_4, C_2, and H_2, but the flow rate might reach a maximum when the temperature range is 500–550 °C.

Aarsen et al. [171] reported that the reaction rate might be controlled by the rate of heat transfer, instead of the kinetics of the reactions, and that this is the result of the higher temperature. In agreement with this statement, Fernández et al. [172] showed that using a reactor with high temperature and long gas residence times decreases tar production, but increases char formation as a result of the extension of the secondary reactions. Agreement between the researchers is that gas residence time and temperature should be higher, but that HR might still need to be investigated. Table 9 illustrates different operating conditions in a pyrolytic reactor for target productions [28].

3.5. Influence of temperature on hydrogen yield

Many researchers from different establishments have investigated the temperature effect on biomass during pyrolysis. Pyrolysis temperature is defined as the heating of a fuel particle at a defined rate from the ambient to a maximum temperature. This temperature importantly affects the composition and the yield of the products. Morf et al. [173] indicated that the amounts of poly-aromatic hydrocarbons were negligible when the pyrolysis temperature was below 500 °C and an important increase in their yields took place at temperatures above 700 °C, indicating that higher temperatures give rise to higher amounts of hydrogen.

Generally, pyrolysis produces three modes of products via the breaking down of heavier complex molecules into smaller molecules, such as solid (mostly char or carbon), liquid (tars, heavier hydrocarbon and water) and gas (H_2, CO_2, H_2O CO, C_2H_2, C_2H_4, C_2H_6, C_6H_6, etc.). The concentrations and characteristics of each product can vary considerably according to the feed characteristics and the operating conditions of the pyrolysis process. The pyrolysis gaseous products contain more than 86 vol% concentrations of LHGs and these promising products either could be reformed to produce hydrogen or can be used as a chemical feedstock or a fuel source to power [29]. Through the primary decomposition of biomass, condensable vapor and NCGs are formed. The vapors are made up of heavier molecules that condense, resulting in additional liquid products. Lower molecular-weight gases, which are generally known as NCGs (CO_2, H_2O CO, C_2H_2, C_2H_4, C_2H_6, C_6H_6) do not condense on cooling. Moreover, a significant amount of NCGs is formed due to the secondary cracking of the vapor. As a result, the final NCG products are the combination of both the primary and secondary gases.

The secondary cracking of pyrolysis vapors increases the gas components when the process temperature is high [29]. In the presence of an equilibrium catalyst, Ioannidou et al. [117] observed the temperature effect on the concentration of CO, H_2, CH_4, and CO_2 produced from corn cob and corn stalk in the captive sample reactor (Figs. 4 and 5). They also studied the same parametric effect in a fixed bed reactor without catalyst (Figs. 6 and 7).

It can be seen from Fig. 4 that the H_2 formation was slightly less than CO at a temperature of 360 °C. In addition, when the

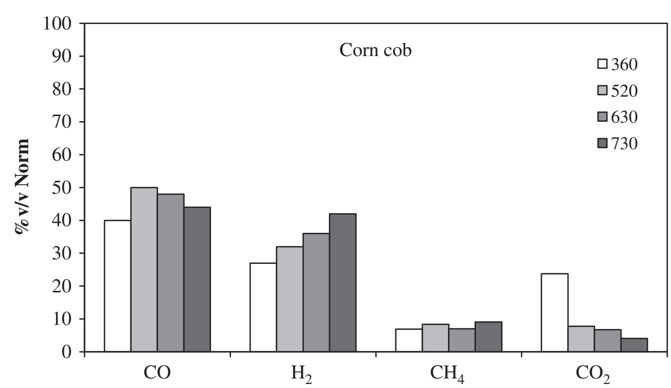


Fig. 4. Temperature effect on the concentration of CO, H_2, CH_4 and CO_2 produced from corn cob in the captive sample reactor in presence of catalyst [117].

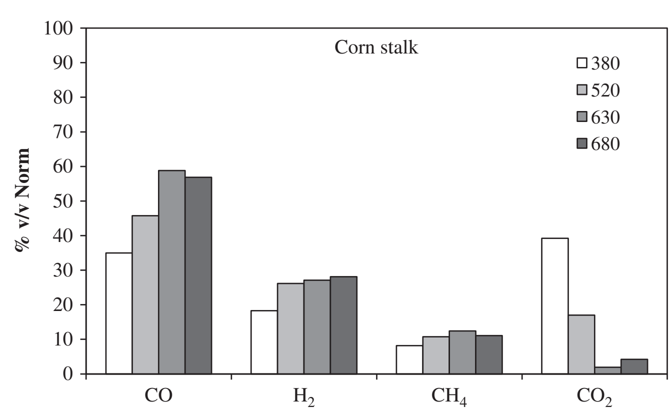


Fig. 5. Temperature effect on the concentration of CO, H_2, CH_4 and CO_2 produced from corn stalk in the captive sample reactor in presence of catalyst [117].

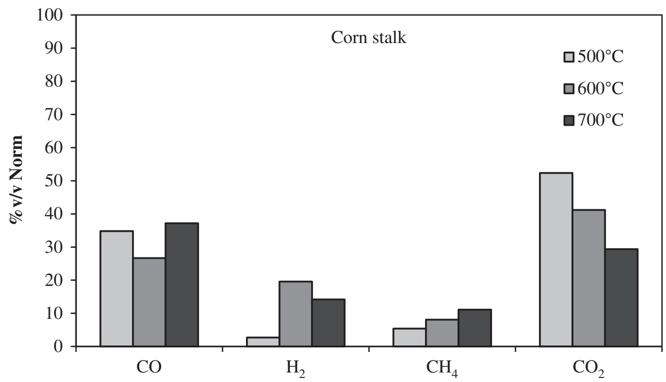


Fig. 6. Temperature effect on the concentration of CO, H_2, CH_4 and CO_2 produced from corn stalk in the captive sample reactor without catalyst [117].

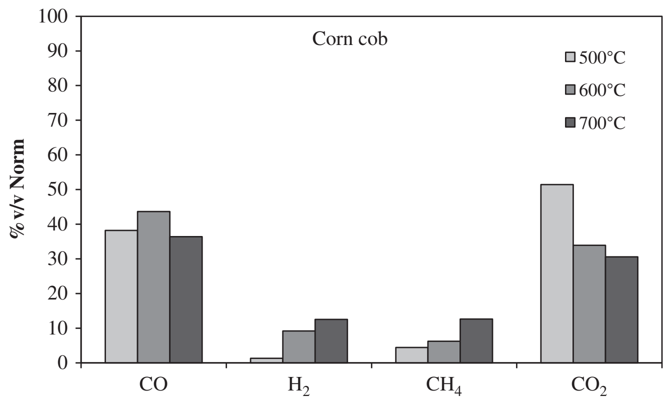


Fig.7. Temperature effect on the concentration of CO, H_2, CH_4 and CO_2 produced from corn cob in the captive sample reactor without catalyst [117].

temperature was increased from 360 to 730 °C, the formation of both hydrogen and CO was increased and that of CO_2 decreased. On the other hand, at 380 °C, the formation of both CO and CO_2 was higher, but the H_2 formation was lower for corn stalk (Fig. 5). Moreover, if the temperature is increased, then H_2 formation increases as CO_2 decreases [158].

Ioannidou et al. [117] showed that the lower heating value (LHV) of gas is typically ranged between 10–13 MJ/m^3 and 13–15 MJ/m^3 for corn cob and corn stalk, respectively, in the captive reactor. Owing to limitations of data regarding gaseous products at 350 °C and below, only a small percentage of NCGs was seen to be produced through the different processes. Lam et al. [29] studied the thermal effect on the secondary cracking of the primary volatiles. They demonstrated that the secondary cracking of primary volatiles resulted from higher thermal energy, which enhanced the cleavage of heavier hydrocarbon chains that are present within the pyrolyzed vapors. Thus, higher yields of pyrolysis gases would be achieved. Above 550 °C, char quantity increased and enhanced the secondary reaction rates. Additionally, the amount of char production decreased if the temperature was increased above 600 °C because of the release of compounds with high boiling points.

Furness et al. [142] described the gas decomposition with briefly and designated the pyrolysis process into a three stages. In the first stage (when temperature was 250 °C), CH_4, CO_2, H_2O were the main pyrolytic products. At second stage (when temperature was 350 °C), hydrocarbon and alcohols were the main pyrolytic products. In third stage (when temperature was 550 °C), H_2, CH_4, CO, CO_2, hydrocarbon and alcohols were main dominating products. The calorific value of those gaseous products was 23 MJ/m^3 and the gaseous components of the pyrolysis products increased with increased temperature [142]. Williams et al. [174] reported that the concentrations of CO and CO_2 increased with pyrolysis temperature and hydrocarbon for biomass pyrolysis in a fluidized bed reactor. The concentration of CO_2 decreased with reactor temperature, whereas the H_2, CO and CH_4 concentration increased [157]. Fig. 8 shows the effect of reactor temperature on dry gas compositions from biomass pyrolysis [120].

The yield of gaseous products increase linearly with increased pyrolysis temperature, whereas solid char formation is reduced at 500 °C during pyrolysis of wood sawdust [175]. The yield of pyrolysis gases is enhanced due to the cracking of hydrocarbons into smaller fragments at higher temperatures. The liquid products transform into gaseous state due to the cracking of hydrocarbons at higher pressure at temperatures of 500–550 °C. The rate of gas flow out of the reactor is rapid because at higher temperatures molecules enter the gaseous phase as early as possible. Greater thermal energy is observable above 550 °C, which increased the secondary cracking and caused more pyrolysis-gas to form. In addition, secondary cracking of primary volatiles should increase due to this higher thermal energy and it is responsible for the cleavage of heavier hydrocarbon chains that present earlier in the vapor and therefore, increasing amounts of pyrolysis-gases form. Furthermore, a higher secondary cracking rate is considered for greater char generation at these high temperatures [13].

However, with increasing temperature, the time for attaining the least conversion level is reduced. By thermal decomposition, the solid biomass turns into gaseous form, such as H_2, CO, CO_2, CH_4, H_2O, and other gaseous hydrocarbons [176]. At 1000 °C, the woody biomass by fast pyrolysis resulting more H_2, CO, CO_2 CH_4, H_2O and other gaseous hydrocarbons than that of char [112]. On the other hand, gaseous products like H_2, CO, CO_2 CH_4, H_2O and light species are formed by the gasification between 800 and 850 °C [26]. Secondary cracking of pyrolysis vapors at higher temperatures cause greater production of gaseous products [177]. Moreover, decomposition of char at higher temperatures significantly increases NCGs, resulting in a net increase of the gaseous products produced. Baumlin et al. [178] investigated whether the biomass thermal process produces higher amounts of gas under higher temperatures. Under higher pyrolysis temperatures, there is more liquid cracking, which results in a greater yield of gaseous products and a lower yield of tar and/or char [179]. Prolonging the reaction time promotes secondary reactions and increases the formation of synthesis gas and LHGs such as CH_4, C_2H_6, etc. The yield of gaseous products as well as the degree of secondary cracking depends on time–temperature functions.

The average molecular weight of the liquid products decreases at temperatures lower than 400 °C, when secondary condensation reactions occur. The average molecular weight reduces with an increase in the degree of secondary reactions if the residence time and temperature are raised [180] and hydrogen production is enhanced with temperature [20,39]. At temperatures of 900 °C in a reactor, hydrogen formation could reach up to 71 g H_2/kg biomass [20]. An outstanding work was outlined by Zuo et al. [164]. For maximum amounts of CO, CO_2 and H_2 gas generation, the pyrolysis temperature is reduced significantly by the addition of phosphoric acid and the process parameters affect greatly the gas release. In addition, phosphoric acid not only promotes H_2 formation, but it also depresses appreciably the CO, CO_2 and CH_4 formation during fir wood pyrolysis with phosphoric acid. They also outlined that the phosphoric acid was used with varying concentrations, but that the process needs a high heating rate. Depending on the operating conditions of the reported experiments, the heavy hydrocarbons are shown to reform as the temperature is varied. If the reactor temperature increases, the yield of gaseous products

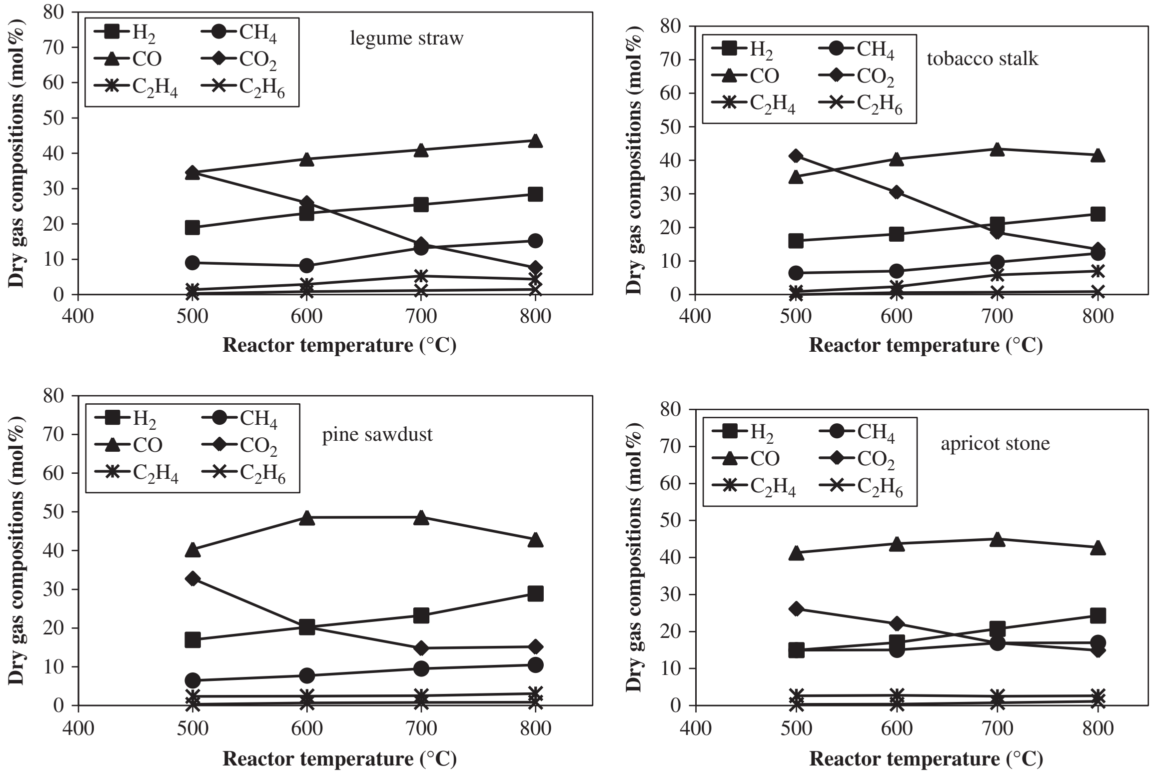


Fig. 8. Influence of temperature on dry gas compositions.

from maple sawdust increases as the temperature increases, and the formation of the liquid and solid products decline [181]. This might be explained by the thermal cracking of hydrogen that happens at high temperatures. The driving force, which is the temperature gradient between the particle and the environment, is proportional to the energy flux. As a result, heat flux and the heating rate are higher when the temperature is high. More accurately, the yield of gaseous products escalates as the char decreases if a higher HR is applied. The synopsis of this section argues that the yield of hydrocarbon gases is promoted if the thermal cracking of the secondary reactions occurs at higher temperatures [182].

3.6. Influence of reactor system on hydrogen yield

Numerous investigations have been conducted for maximizing production of hydrogen by observing the effects of the reactor during pyrolysis as a consequence of temperature. The heating rate, pyrolysis temperature and the duration of pyrolysis should be chosen appropriately, when the purpose of the pyrolysis is to form the optimal amount of gas. The reactor configuration shows the rapid influence of the secondary reaction kinetics and the formation of hydrogen, which depends on the time–temperature profile of the pyrolysis process, as reported by Bridgwater [136]. As pyrolysis is a precursor to both combustion and gasification, the same reactors can be used for the pyrolysis process. Depending on the feedstock and the heating mode, the pyrolysis reactor can be classified, such that the thermochemical conversion of biomass into hydrogen and NCGs is easily obtained at the maximum amount. The prevailing reactor conditions, for example, the external heat transfer co-efficient, is dependent on the feedstock type and the dimensions of the many reactor types, such as fluidized bed, fixed bed, ablative, cyclonic, rotating transported, screw reactors, etc. [183]. However, Ni et al. [24] reported that hydrogen production from biomass pyrolysis using fluidized bed reactors would be attained at a higher production rate due to it exhibiting higher heating rates.

Suitable reactors are outlined in Table 10 and some crucial advantages and disadvantages are revealed in Table 11. It can be seen from these two tables that the ultimate products from biomass conversion depend solely on reactor design and operating conditions. It can be concluded from these two tables that the ultimate outcome of the pyrolysis process is dependent on the selection of the appropriate reactor and feedstock type. Once both of these parameters are settled in full range the others parameters should be carried out in such a way that heat-transfer mechanisms within the reactor favors the higher residence time [183].

3.7. Influence of carrier gas on hydrogen yield

The key role of the carrier gas (CG) is to remove the volatiles from the pyrolysis environment during the biomass pyrolysis process. Usually CGs like nitrogen, CO_2, steam, and hydrogen are used during biomass pyrolysis. The biomass particles used in the process are larger than millimeter size. As a result, there might be significant mass transfer resistance for the organic volatiles from the feedstock. Longer residence times at high temperatures favor the secondary pyrolysis reactions, resulting in higher gaseous products with nitrogen flow rates as CG, as was outlined by Şensöz et al. [121]. If the purpose was to produce maximum gaseous products, then secondary reactions, such as thermal cracking, re-polymerization and re-condensation must be kept at a maximum because the CG removes the volatiles from the pyrolysis environment [199]. The residence time of the pyrolysis products is a function of N_2 purge and feedstock rates. If N_2 CG rates are higher, pyrolysis-volatiles escape from the reaction zone due to the higher pressure created in the reactor. On the other hand, the lower residence time increases the formation of liquid oil, lowering the gas formation [29]. Abnisa et al. [113] discovered that the char formation is reduced significantly when a nitrogen stream is

Table 10
Influence of reactor system on products formations.

Reactor Name	Reactor arrangements	Heating source	Biomass feed	Operating variables	Hydrogen yield (%)	Light gaseous yield (%)	Total gas yield (%)	Ref.
EFR	Made up of alumina tube	EF	Sylvester pine wood Spruce wood	*T*: 1073–1273 K HR: 500 K/s PS: 0.4–1.1 mm RT: 0.7–3.5	20	CO: 40; CO_2: 5; CH_4: 10; C_2H_4: 5	70	[184][a]
FBR	Made up of stainless steel; height 800 mm; inner diameter 20 mm	EF	Sawdust	*T*: 850 °C *P*: 1 atm	81.1	N/A	N/A	[185][b]
FR	Made up of 1 Cr18Ni9Ti stainless steel pipe; height 1400 mm; bed diameter 40 mm; freeboard diameter 60 mm	EF	Pine sawdust	*T*: 900 °C *P*: 1 bar	71	CO: 40; CO_2: 20; CH_4: 8; C_2H_6: 0.15; C_2H_4: 3	N/A	[186][c]
FBR	Made up of high-temperature stainless steel; height of the reactor 71.2 cm; Inner diameter 12.52 mm	EF	Bio-oil	*T*: 600 °C *P*: 1 bar	90	N/A	N/A	[187][b]
EFR	Made up of straight tube; height 60 cm or 120 cm	EF	Wheat straw	*T*: 900 °C RT: 150–250 ms	20	CO: 52; CO_2: 8; CH_4: 11; C_2H_6: 2; C_2H_4: 5	91	[188]
TR	Made up of stainless steel cylinder; height 0.75 m; inner diameter 2.2×10^{-2} m	EF	Kraft lignin Organocell Lignin	*T*: 800 K	50	CO: 33–44; CO_2: 12-2; CH_4+C_2H_6+C_2H_4: 1–6	N/A	[178][a]
DTR	Made up of alumina tube; height 2.3 m; inner diameter 0.075 m	EF	Commercial beech	*T*: 1600 °C *P*: 1 atm	2.5	CO: 4; CO_2: 12; CH_4: 6; C_2H_6: 1; C_2H_4: 1.5	N/A	[112][d]
FBR	N/A	EF	Wheat straw	*T*: 450 °C CGFR: 0.75–1.79 m^3/h	14	CO: 5–7; CO_2:15–20; CH_4: 12	22	[43]
FBR	Made up of stainless steel tube, Inner diameter 1.65 cm; height 42.6 cm	EF	Bio-oil	*T*: 800 °C	85	N/A	N/A	[189][b]
FBR	Made up of 316-l stainless steel tube; outer diameter 12.7 mm	EF	Sunflower oil	*T*: 800 °C	72.87	CO: 18.1; CO_2: 10.7; CH_4: 13.4; C_2H_6: 3.2; C_2H_4: 39.1	N/A	[58][b]
FFR	N/A	EF	Legume straw	*T*: 800 °C PS: 0.45–0.90 mm	28.2	CO: 38.5; CO_2: 15; CH_4: 18; C_2H_6: 5; C_2H_4: 8	N/A	[44][a]
PBR	Made up of stainless steel; diameter 125 mm, height 500 mm	EF	Waste wood	*T*: 650 °C HR: 10 °C/min	7	CO: 30.5; CO_2: 44.7;CH_4: 14.7	41.3	[190][b]
FR	Made up by 1Cr18Ni9Ti stainless steel; height1200 mm outer diameter 100 mm	Sandy particle	Sawdust	*T*: 750–860 °C *P*: 1 atm	9.27	CO: 9.25;CH_4: 4.21; C_2H_6: 0.25; C_2H_4: 0.65	N/A	[119]
BFR	Inner diameter 0.15 m; height 2.15 m; bed material ofite	EF	Wood pellet	FR:10–21.6 kg/h GA: air+oxygen +steam *T*: 755–840 °C	25.7	CO:28.5; CO_2: 9.2; CH_4: 8.1	N/A	[191][a]
BFR	Made up by stainless steel tubes; inner diameter 140 mm; height 1010 mm; bed material quartz, olivine, dolomite and Ni-alumina	EF	Spruce wood pellet	FR: 0.75 kg/h with N_2 GA: air+steam *T*: 780 °C ER: 0.17	30.3	CO: 17.6; CO_2: 14.3; CH_4: 1.49; C_nH_m: 0.02	1.20	[192][a]
BFR	Made up by 1Cr18Ni9Ti stainless steel; inner diameter 40 mm; height 1400 mm	EF	Pine sawdust	FR: 0.47 kg/h GA: air BT: 800 °C ER: 0.3	38.38	CO: 24.89; CO_2: 27.62; CH_4: 7.02; C_nH_m: 2.09	1.56	[193]
BFR	Made up by stainless steel; inner diameter 4.2 cm; height 57.5 cm	EF	Larch wood	FR: 0.21 g/min GA: steam *T*: 650 °C or 750 °C	55.97	CO: 7.71; CO_2: 29.23; CH_4: 5.72; C_nH_m: 1.38	1.54	[194]
BFR	Inner diameter 60 mm; height 90 mm; bed material olivine	EF	Olive kernel	FR: 120 g/min GA: air *T*: 750–850 °C ER: 0.2–0.4	23.98	CO: 14.26; CO_2: 19.42; CH_4: 3.75; C_nH_m: 1.81	N/A	[195]
BFR	Inner diameter (bottom: 1.4 m; top: 2 mm); height 8.5 m	EF	Rice husk	FR: 400–1500 kg/h	5–8	CO: 16–21; CO_2: 15–16; CH_4: 4–6; C_nH_m: 2	N/A	[196][b]

Table 10 (*continued*)

Reactor Name	Reactor arrangements	Heating source	Biomass feed	Operating variables	Hydrogen yield (%)	Light gaseous yield (%)	Total gas yield (%)	Ref.
				GA: air T: 680–810 °C ER: 0.18–0.27				
BFR	Made up by stainless steel; inner diameter 10 cm; height 92 cm	EF	Coconut shell	FR: 0.5 g/min GA: steam BT: 600–800 °C Steam/C: 0.2–1	38.74	CO: 35.72; CO_2: 29.9; CH_4: 4.5	N/A	[197]
CFR	Height 4000 mm; inner diameter 410 mm	EF	Wood powder	FR: 210 kg/h GA: air *T*: 630–1042 °C ER: 0.17–0.28	16.32	CO: 16.7; CO_2: 15.6; CH_4: 6.9; C_nH_m: 1	1.927	[198][b]

"EFR, FR, FBR,TR, DTR, FFR, PBR, BFR and CFR": Represents Entrained flow reactor, Fluidized reactor, Fixed bed reactor, Tubular reactor, Drop tube reactor, Free-fall reactor, Packed bed reactor, Bubbling fluidized reactor and Circulating fluidized reactor respectively.
"a, b, c and d": References measured the gas yield in the basis of mol%, percentage (%), g H_2/kg biomass and wt% respectively while rest of the gas yield measured in vol% basis.
"EF, T, P, HR, PS, RT, CGFR, GA, FR and ER": Represents electrical furnace, temperature, pressure, heating rate, particle size, residence time, carrier gas flow rate, gasification agent, flow rate and equivalence ratio respectively.
"N/A": Not available.

used as a CG, because this gas removes uncondensed volatiles from the reaction zone; therefore, gas formation is enhanced when the nitrogen flow rate is high. With regard to the expected LHG products, the most probable light species are CO, CO_2, H_2, C_2H_4, and CH_4.

The evolution of gaseous products is enhanced if the N_2 stream flow rate is high, which leads to a reduction of the liquid oil production. Moreover, N_2 purge rate not only reduces the partial pressure of the volatiles, but it could lessen the condensation of the pyrolysis-volatiles into the pyrolysis-oil, because a large amount of the N_2 stream is present in the vapor phase. Such results create significant heat within the reactor, which leads to secondary decomposition of the primary pyrolysis-products and promotes gaseous product formation. A decrease in the N_2 purge rate enhances either the volatiles residence time or the H_2 and CO contents, as well as reduces the aliphatic content in the pyrolysis-gases. As a result, the residence time promotes secondary reactions of the hydrocarbon in the volatiles, because the aliphatic content converts into smaller hydrocarbon chains. Furthermore, a longer residence time not only improves the heterogeneous reactions between the carbon and the pyrolysis volatiles in the reactor, but it could also transform a part of the aliphatic content into gaseous products, e.g., H_2 and CO.

The hydrogen and the total gas formation were enhanced and decreased, respectively with an increased flow rate of the carrier gas at a constant heating rate. For example, the Kraft lignin pyrolysis can be found with a decreased formation of gas products ranging from 820 to 736 ml/gm when the carrier gas is increased from 13.4 to 33 ml/min/g of lignin at 800 °C with a constant heating rate of 15 °C/min. On the other hand, hydrogen formation increased from 43 to 66 mol%, while an increase from 31 to 46 mol% can be found for Alcell lignin. The products from Alcell lignin pyrolysis decreased from 820 to 762 ml/g at 800 °C with a constant heating rate of 15 °C/min [200]. However, methane and other hydrocarbon yields decreased with steam flow rate owing to the further reaction of methane via steam reforming and partial oxidation reactions. In addition, Lv et al. [57] pointed out that the formation of the HG and CO increased from 31.84–32.10 mol% and 34.19–37.73 mol% respectively when the steam flow rate changed from 0.27 to 1.2 kg/h during the pyrolytic conversion of pine sawdust at 800 °C.

An increased production of hydrogen and gaseous products during pyrolysis is expected as the CG velocity if decreased, because the residence time of the volatiles in the reactor is enhanced; hence, increasing the formation of secondary reactions [152]. The char formation is reduced significantly when longer residence times of volatile matter are applied over Na_2CO_3-impregnated cellulose. The abstract from such impregnation is that more LHGs form due to the primary volatiles following the secondary reactions through competitive pathways [201]. Another prediction was that with varying particle size, there would be no obvious influence on the yield of pyrolysis products, especially bio-fuel, as the rate of nitrogen increased [152].

3.8. *Influence of catalysts on hydrogen yield*

It can be seen that much concerted effort has been made in the past to determine the quality and chemical composition of the pyrolysis gases. To support this gas quality, catalysts were supposed to be the crucial parameter. In order to achieve low pyrolysis temperature, high chemical and physical stability, and high yields of components, catalysts can be considered as very important [202]. In production of hydrogen and gas species, the problem is that the char and tar formation. To solve this problem, catalyst could be applied because it is not only mitigates the tar content but also enhance the gas product quality and conversion

Table 11
Advantages and disadvantages of some reactors [136].

Reactor Type	Advantages	Disadvantages
Ablative reactor	Feeding large feedstocks CG is not necessary Mechanical char abrasion from biomass is very high Higher motion between particle and reactor wall Installation of condensation units with a small volume, resulting less space at low cost	Copmact pattern Heat supply is more complex Scalling is more costly
Circulating fluid bed reactor	Heat transfer rate is high Mechanical char abrasion from biomass is very high and char erosion causing 1% radiation high char in product Maximum size of the particle up to 6 mm Possibility of liquids cracking by hot solids Possibility of catalytic activity from hot char; Possibility of greater reactor wear	Requiring char/solid heat carrier separation Requiring solids recycle
Fluidized bed reactor	Heat transfer rate is high Directly heat supply to fluidizing gas or to bed Very good solids mixing; PS limit <2 mm in smallest dimension Simple reactor configuration	Limited char abrasion
Entrained flow reactor	Low heat transfer rates PS limit <2 mm Limited gas/solid mixing Simple design	High cost for feed preparation
Fixed bed reactor	Slow heat transfer rates Uniform PS Relatively clean gas produced	
Vacuum furnace reactor	Higher RT Short vapor residence time Larger feed stock required No CG is needed	Process is mechanically complicated
Rotating cone reactor	Higher heat transfer rate Short residence time of the solid CG requirement is less	Raising scaling issues when the geometry of system is complex
Auger reactor	Controlling of biomass RT is easy Condense size Requiring absence of CG Requiring low processing temperature (400 °C)	Presence of moving part of hot zone Heat transfer at larger-scale

"CG, PS, and RT": Represents carrier gas; particle size and residence time respectively.

potentiality [24]. There are several kinds of potential catalyst that could be used for the production of hydrogen and gaseous components, such as inorganic salts (chlorides, carbonates and chromates) [24,38], nickel-based catalyst [203], and metal oxides [39,203].

Catalyst can be placed inside the pyrolysis reactor in the layer of glass wool or it can be dry mixed with feedstock biomass. If a catalyst is used for biomass pyrolysis, the liquid yield would be reduced and the gas yield increased [204]. If the catalytic temperature is increased, hydrogen and hydrocarbon concentration of the gases is also increased [174]. For example, rice husks at 550 °C yield 25.4 wt% gas, but by applying catalysts a tremendous increase (22.2–41 wt% gas) in the trend of gas formation could be observed from 400 to 600 °C. Aside from such characteristics, Mathews et al. [205] showed that the formation of gases such as C_3 was reduced when the reactor temperature increased. On the other hand, the Al-MCM-41 catalysts reduced carbonyls and acid formation during biomass-based fast pyrolysis vapors, when subsequently it also demonstrated formation of hydrocarbons, phenols and poly-aromatic hydrocarbons in a fixed bed [206].

It can be seen that generally, hydrocarbon comes from alkane and alkene gases when zeolite catalysts are applied for upgrading the biomass-pyrolysis-derived oil [207]. Thangalazhy-Gopakumar et al. [86] demonstrated that if the catalyst loading was boosted from two to five times, there was no significant increase shown by the hydrocarbons when using zeolite catalysts during biomass pyrolysis. Evidently, the HZSM-5 zeolite catalysts could be maximizing the hydrocarbons by converting bio-oil and hence, generating a smaller amount of acidic silica-alumina with non-acidic silicalite during improving bio-oils in a fixed bed micro-reactor by fast pyrolysis with different catalysts [208]. By using Ni-based catalyst, hydrogen formation of u to 90% could be attained [209]. Anis et al. [210] showed that by using Ni-based catalysts, space velocity expressed little effect on gas composition, but hydrogen production is enhanced and tar is reduced by 99% when the temperature is increased. Rapagnà et al. [211] showed that fresh Ni catalysts demonstrated the potential to yield 62.1 vol % of hydrogen at 830 °C using a fluidized bed reactor by catalytic biomass steam gasification.

Chattanathan et al. [212] reported that the H_2 and CO_2 yields were low in the absence of Ni–Al catalysts, and showed that the total gas yield decreased with a decrease in catalyst weight. In addition, Czernik et al. [213] and Kechagiopoulos et al. [187] used a nickel-based naphtha reforming catalyst to produce hydrogen. Kechagiopoulos et al. [187] used a C11-NK catalyst, which has higher potassium content compared with other Ni catalysts. The higher potassium content plays a vital role in suppressing the coke formation and a 90% hydrogen yield was reported for the equimolar mixture of model compounds [187]. On the other hand, Wang et al. [214] conducted reforming over three catalysts: C12A7/15% Mg, 12% Ni/gamma-Al_2O_3, and 1% Pt/gamma-Al_2O_3 at 650 °C and the observed hydrogen yields were 56.7%, 58.1%, and 66.8%, respectively. Yan et al. [215] reformed bio-oil with a commercial Z417 catalyst along with CO_2 sequestration using calcined dolomite and reported a hydrogen yield of about 75%. Wu et al. [48] carried out a steam pyrolysis-gasification of wood

Table 12
Influence of oxide catalysts on hydrogen production [20].

Catalysts name	Yielding of hydrogen (per μmol)
None	90
CeO	263
MgO	430
TiO_2	560
ZrO_2	490
Al_2O_3	480
SiO_2	230
Rh/CeO_2	1290
Ru/CeO_2	1101
Pd/CeO_2	830
Pt/CeO_2	850
Ni/CeO_2	740
G-917	60
Rh/TiO_2	800
Rh/MgO	820
Rh/SiO_2	720

sawdust with a Ni/MCM-41 catalyst for hydrogen production in a two-stage fixed bed reaction system. Hydrogen production was increased from 30.1 to 50.6 vol% when the Ni loading was increased from 5 to 40 wt%. The use of Ni catalysts produced hydrogen of 73% at 950 °C during the bio-oil upgrading in a fixed bed reactor [216].

Catalyst load has an effect on the hydrogen and NCGs production by pyrolysis process. Chen et al. [39] found that if the catalyst load is lower, then the catalyst shows greater potential for hydrogen and NCGs. They also reported that for rice straw pyrolysis, Na_2CO_3 showed a stronger effect than $CaCO_3$, while for olive husk pyrolysis, K_2CO_3 demonstrated a higher effect than Na_2CO_3. Demirbaş [38] pointed out that yields of hydrogen and NCGs are increased in the presence of a $ZnCl_2$ catalyst, and they showed that the highest yield of hydrogen-rich gas (about 70.3%) was obtained from olive husks using about 13% $ZnCl_2$ at 1025 K. The catalytic effect of Na_2CO_3 was stronger than that of K_2CO_3 for the cotton cocoon shell and tea-waste, but the effect of K_2CO_3 is very severe on olive husks. Compared with the noble metals, such as Ru, Rh and Pt, those are more effective and less susceptible to carbon formation and comparable with Ni catalysts, but owing to the high cost, they are not generally used [217]. On the other hand, several types of oxide catalyst have attracted R&D attention and of these, CeO_2 has achieved the best results. For example, in cedar wood biomass pyrolysis, 98% of gaseous products are produced using $Rh/CeO_2/SiO_2$ catalyst [20]. Table 12 demonstrates the efficiency of several catalysts on hydrogen formation.

Among all other metal oxides, Al_2O_3 and Cr_2O_3 appear to have a strongest catalytic role, as highlighted by Ni et al. [24]. For biomass cracking, ZSM-5 zeolite catalysts are frequently used rather than other zeolite catalysts. Zeolite catalysts provide excellent activity, shape selectivity to hydrocarbon, limited deactivation by coke, and high thermal stability [218]. Using ZSM-5 zeolite catalysts not only reduces liquid products, but also increases the formation of gaseous products [219].

4. Conclusion

This paper has investigated a sustainable hydrogen energy future, which relies on technologies that abolish carbon issues from the energy equation and reduce the emission of greenhouse gases that are detrimental to the atmosphere. Several process parameters that affect this farsighted energy source have been outlined, and it has been shown how to maximize the hydrogen formation, together with its co-products, which are the permanent gases, such as CO and CO_2 and light hydrocarbons, such as CH_4, C_2H_4, and C_2H_6. Snapshots of the different pyrolysis processes have been summarized, which indicate that the process selection depends on the interest in the products ultimately formed. It is seen that moisture could affect the generation of hydrogen and non-condensable gases in such a way that heightens the overall production of the net products. Cellulose and hemicellulose components are easily degraded into low molecular weight species at a given temperature, whereas lignin has the tendency to show the opposite trend due to internal bonding mechanisms. It is very puzzling that the formation of hydrogen and non-condensable gases either increases or decreases with thermal conductivity, and this argument is varied between most of the researchers. Longer residence times at high temperatures favor the secondary pyrolysis reactions, resulting in higher gaseous products with nitrogen flow rates as the purge gas. Particle sizes have applications in increasing the formation of hydrogen and the non-condensable gases. Although much of the study investigated the impact that catalysts have on the pyrolysis process, it is apparent that Ni-based catalysts and zeolite-based catalysts have demonstrated the greatest potential for improving the gas quality and for extracting the maximum gas production. However, it is apparent from the literature that hydrogen generation through pyrolysis still has many obstacles to overcome as follows: (1) volatile composition, (2) separations and purifications, (3) production cost, (4) selection of catalyst or other material that ease the equilibrium of the process, and (5) availability of sustainable biomass.

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